Molecular Simulation of Adsorption and Desorption in Disordered Porous Materials via Diffusive Mass Transfer

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In this work we use molecular modeling to study adsorption and desorption in disordered porous materials via computer simulation methods. Our aim is to gain a better understanding of the relationship between adsorption isotherms and microstructure of porous materials such as silica xerogels. The molecular models used in this work have elements of the complex three dimensional microstructure of real materials. In particular the adsorption isotherms and capillary phase diagrams exhibit features that cannot be understood in terms of a collection of single pores with simple geometries. The adsorption/desorption isotherms obtained via grand canonical Monte Carlo (GCMC) simulations exhibit hysteresis which resembles that seen experimentally. The origin of the hysteresis is metastability of the low and high density phases of the adsorbate, and does not appear to be related to pore blocking phenomena which are often used to explain hysteresis. However, since the mechanism of adsorption and desorption in GCMC simulations is different from that in experiments the question arises as to whether the hysteresis in the simulations can be used to model that seen experimentally. In order to investigate this issue further we have developed an alternative simulation strategy based on the grand canonical molecular dynamics with a control volume (GCMDCV) developed by van Swol and coworkers. In this approach the system is divided into two subvolumes. The system is then simulated via GCMDCV with one of the subvolumes serving as the control volume. Adsorption/desorption into the other subvolume can only occur via diffusive mass transfer and this more closely mimics the experimental situation. Results obtained so far with this method both for bulk systems and fluids in disordered porous materials indicate that adsorption/desorption hysteresis obtained via the GCMDCV approach is similar to that seen in GCMC simulations. This would suggest that given an appropriate model for the porous material microstructure GCMC simulation can yield useful information about hysteresis phenomena in adsorption.